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Haddad, Timothy S.; Moore, Brian; and Phillips, Shawn H. (ERC), "Synthesis and Characterization of a New (Tetrasilanol) Cyclosiloxane"

SYNTHESIS AND CHARACTERIZATION OF A NEW (TETRASILANOL)CYCLOSILOXANE

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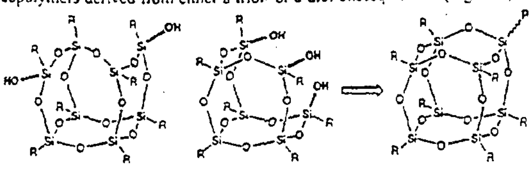
Introduction

There has been recent interest in using incompletely condensed silsesquioxanes as molecular building blocks in many polymer systems.[1] This interest is driven by significant property enhancements imparted by inclusion of a nanosized inorganic particulate into an organic matrix. Most of the work to date has focused on thermoplastic hybrid inorganic/organic copolymers derived from either a triol- or a diol-silsesquioxane (Figure 1).

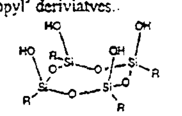


A disilanol directly useful for producing thermoplastic AB copolymers

A trisilanol can be easily converted into a macromer containing a single polymerizable functionality

Figure 1. Two types of incompletely condensed silsesquioxanes used for making hybrid inorganic/organic materials.

There is a need for the development of other incompletely condensed silsesquioxanes useful in both thermoplastics and thermosets. Towards this end, we have been studying the isolation and chemisty of a new cyclosiloxane containing four silanol functionalities. This tetrasilanol is tentatively assigned the structure shown in Figure 2 which is analogous to the known phenyl[2] and isopropyl[3] deriviatves.



R = cyclopentyl, 1
phenyl
i-propyl

Figure 2. Incompletely condensed tetrasilanols. The X-ray crystal structures of the phenyl and isopropyl derivatives have been solved.

Experimental

Materials. Cyclopentyltrichlorosilane and dimethylchlorosilane were purchased from United Chemical Technologies. Technical grade acetone and deionized water were used as received. Tetrahydrofuran was dried by passage through an activated alumina column and triethylamine was distilled from sodium.

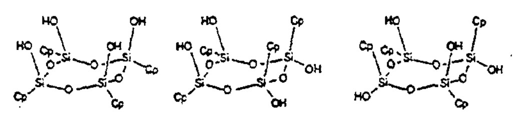
Instrumentation. ^{1}H, ^{13}C, ^{29}Si NMR spectra were obtained on a Bruker AMX-300 spectrometer using 5 mm o.d. tubes. Sample concentrations were about 10% (w/v) in either $CDCl_3$ or d_6-acetone and were referenced internally to the solvent.

Synthesis of 1,3,5,7-(tetrahydroxy)-1,3,5,7-(tetracyclopentyl)cyclotetrasiloxane, 1. To a 1000 mL erlenmeyer flask equipped with a stirbar and containing 600 mL of cold deionized water, a cyclopentyltrichlorosilane (12.54 g, 61.6 mmol) acetone solution (50 mL) was added in a dropwise manner over a period of one hour. Once the addition was complete, the stirbar was removed, rinsed with a few mLs of acetone and the reaction flask sealed. After 2 weeks a white precipitate was obtained by filtration (7.10 g, approximately 89 % yield) that contained two main products as revealed by ^{29}Si NMR (singlets at -44.2 and -53.2 ppm along with minor peaks at -44.5 and -53.8 ppm). Extraction of this precipitate with acetone, filtration, solvent reduction and precipitation into water purifies the desired product. ^{1}H NMR (d_6-acetone, ppm) 5.40 (s, 1H), 1.76 (mult, 2H), 1.52 (mult, 6H), 0.95 (mult, 1H). ^{13}C{^{1}H} NMR (d_6-acetone, ppm) 28.23 (s), 27.53 (s), 24.28 (s). ^{29}Si{^{1}H} NMR (d_6-acetone, ppm) -53.2 (s).

Synthesis of 1,3,5,7-tetra(dimethylsilyl)-1,3,5,7-tetra(cyclopentyl)-cyclotetrasiloxane. Under a nitrogen atmosphere, a slight excess of dimethylchlorosilane (240 mg, 2.54 mmol) was added to a 15 mL THF solution of triethylamine (260 mg, 2.57 mmol) and 1,3,5,7-(tetrahydroxy)-1,3,5,7-(tetracyclopentyl)cyclotetrasiloxane, 1, (300 mg, 0.576 mmol). The reaction is over within 1 hour as seen by HPLC. The solution was filtered (under air) to remove NEt_3HCl and the solvent removed under vacuum. The residue was extracted with diethylether, refiltered and the solvent removed under vacuum to yield a single compound. ^{1}H NMR ($CDCl_3$, ppm) 4.76 (sept, J = 2.8 Hz, 1H), 1.73 (mult, 2H), 1.51 (mult, 6H), 0.89 (mult, 1H), 0.23 (d, J = 2.8 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm) 27.55 (s), 27.07 (s), 23.66 (s), 0.68 (s). ^{29}Si{^{1}H} NMR ($CDCl_3$, ppm) -5.9 (s), -67.6 (s).

Results and Discussion

The hydrolytic condensation of cyclopentyltrichlorosilane in refluxing 80 % acetone and water produces a high yield of the trisilanol shown in Figure 1, a small amount of a fully condensed octamer, along with some resinous polymer.[4] A change in the solvent composition can result in significant changes to the product distribution. An attempt to produce a tetrasilanoldisiloxane, $[(C_5H_9)Si(OH)_2]_2O$ analogous to a cyclohexyl derivative reported by Brown[5] using about 10 % acetone and 90 % water yielded a mixture of resinous products. However, we found that if the reaction was allowed to proceed for a longer time, a single major product, 1, was produced along with smaller amounts of other partially condensed silsesquioxanes. This major product can be isolated in about 50 % yield; NMR spectroscopy reveals it to be a high symmetry compound containing a single silanol group per silicon. The three reasonable structures that fit all the available data are shown in Figure 3. In the absence of any single crystal X-ray crystallography data, there is no simple way to unambiguously assign the correct structure. However, the analogous compounds with phenyl[2] or with isopropyl[3] groups at silicon are also known and they have been proven to have the all cis-structure by X-ray crystallography.



cis-cis-cis-tetrasilanol 1a cis-trans-cis-tetrasilanol 1b trans-trans-trans-tetrasilanol 1c

Figure 3. Three possible structures for compound 1.

Tetrasilanol **1a** can be derivatized by addition of dimethylchlorosilane to a THF solution of **1a** containing slightly more than four equivalents of NEt_3. The reaction is rapid and quantitative, yielding a high symmetry tetrahydride. NMR spectroscopy reveals a single $SiMe_2H$ moiety per cyclopentyl group consistent with an all cis structure. The hydride functionalities open a manifold of reaction possibilities utilizing hydrosilation chemistry.

Conclusions

A new incompletely condensed silsesquioxane tetraol has been synthesized and characterized. It is easy to derivatize into a tetrafunctional macromer that can be incorporated into thermosets. This work is currently underway.

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